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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to new granular precipitate silicic acid. Especially this invention has comparatively big particle diameter suitable for bulking agents, such as rubber, a plastic, resin, and toothbrushing, and, moreover, has high intensity.

New granular precipitate silicic acid which is hard to powder, and a manufacturing method for the same are provided.

[0002]

[Description of the Prior Art]When an alkaline silicate and mineral acid are roughly classified into the process of the silicic acid used as a raw material, there are a sedimentation method which makes it react by alkalinity and settles silicic acid, and the gel method for making it react with acidity and obtaining hydrogel as an intermediate. The silicic acid obtained by the gel method is generally hard, and is used as a drier, a separating medium, a flattening of a paint, etc. On the other hand, precipitate silicic acid is generally soft and is powder with a high whiteness degree in tasteless no odor with surface activity.

It is used for various fields, such as agricultural chemicals, a paint, resin, an office-use paper, toothbrushing, and foodstuffs addition, including the rubber reinforcing filler.

[0003]

[Problem(s) to be Solved by the Invention]By the way, the needs for precipitate silicic acid with larger particle diameter than before have come out from diversification of a use, and the demand to new physical properties. For example, in cosmetics or toothbrushing, there is a request that the touch, tactile feeling, etc. want to improve using precipitate silicic acid with larger particle diameter than before. In the field as bulking agents, such as rubber, a plastic,

and resin, there is also a request of liking to improve the workability at the time of adding precipitate silicic acid to rubber etc. by using precipitate silicic acid with larger particle diameter than before.

[0004]The particle diameter of the precipitate silicic acid marketed to it until now is mean particle diameter, and, generally is about 1-50 micrometers. However, there is no literature which indicate the art aiming at obtaining precipitate silicic acid whose particle diameter is still larger substantially. However, although it does not aim at originally obtaining large precipitate silicic acid of particle diameter, according to the method currently indicated by JP,62-32129,B and JP,62-153113,A, it is known, for example that precipitate silicic acid of comparatively big particle diameter can be manufactured. These methods make water distribute the humid cake which filtered hydration silicic acid, are made into a slurry, add and carry out spray drying of the weak alkaline compounds, such as sodium carbonate or sodium acetate, to this slurry, and obtain basic precipitate silicic acid.

[0005]Then, this invention person examined the method indicated by above-mentioned JP,62-32129,B and JP,62-153113,A for the purpose of obtaining large precipitate silicic acid of particle diameter. As a result, it turned out that the precipitate silicic acid which has to some extent large particle diameter is obtained by a described method. However, it became clear that there was a tendency which particles are destroyed in the midst of handling, and powders the obtained precipitate silicic acid when it is going to add, for example to rubber etc. When using it in fields, such as cosmetics and toothbrushing, it also turned out that the touch and tactile feeling are insufficient. In these precipitate silicic acid, it also became clear that impurities, such as sodium carbonate and sodium acetate, are also intermingled and that it became a problem depending on a use.

[0006]Then, the purpose of this invention is to provide granular precipitate silicic acid which has comparatively big particle diameter, does not powder during handling, and has the suitable touch and tactile feeling, and a manufacturing method for the same.

[0007]

[Means for Solving the Problem]This invention relates to granular precipitate silicic acid which is in a range whose particle diameter of not less than 60% of particles is 75-250 micrometers by weight conversion, and is characterized by particle strength being the range of 0.1 to 0.3 kgf/mm^2 .

[0008]Furthermore, this invention adds sodium hydroxide or a sodium silicate to suspension of precipitate silicic acid, and relates to a manufacturing method of the aforementioned granular precipitate silicic acid carrying out spray drying of the suspension obtained by adjusting the pH of said suspension to the range of 8.5-11.5. Hereafter, this invention is explained still in detail.

[0009]Precipitate silicic acid of this invention is in a range whose particle diameter of not less than 60% of particles is 75-250 micrometers by weight conversion. As for precipitate silicic acid

of 75 micrometers or less, particle diameter is used in a field that it is called for until now that a state of the surfaces, such as a paint, a special paper, and a film, is comparatively smooth. Although it is that precipitate silicic acid whose particle which is 75 micrometers as particle diameter is small is not less than 60% is not known for this invention to it until now, For example, it found out that it was what can provide cosmetics and toothbrushing with the new touch, tactile feeling, etc., or improves workability as bulking agents, such as rubber, a plastic, and resin. Especially precipitate silicic acid whose particle which is 75 micrometers as particle diameter is small is not less than 70% is suitable for acquiring the above effects. On the other hand, there is a problem of becoming severe with ZARA, in precipitate silicic acid whose particle with particle diameter of greater than 250 micrometers is not less than 60%. Like [in this invention] the after-mentioned in particle diameter, after setting a screen of 250, 200, 150, and 105 or 75-micrometer meshes of a net using a low tap type standard sieve shaker, putting in 50 g of samples and vibrating for 10 minutes, it asks by measuring sample weight of each plus sieve.

[0010]Particle strength of precipitate silicic acid of this invention is the range of 0.1 to 0.3 kgf/mm². If particle strength is more than 0.1 kgf(s)/mm², it will not be substantially powdered during handling. Although it becomes more difficult to powder precipitate silicic acid in which particle strength exceeds 0.3 kgf(s)/mm², it becomes hard too much like silica flour or silica gel, and cannot be used in the use field made into the purpose of this invention. If it is a mentioned range, it is not known until now, but cosmetics and toothbrushing can also be provided with the new touch, tactile feeling, etc., for example. Measurement of particle strength of precipitate silicic acid in this invention is performed by measuring particle strength using a minute compression testing machine (for example, the Shimadzu Corp. make / MCTM-2 type).

[0011]Precipitate silicic acid of this invention has a more preferred thing of a range whose particle in a range whose particle diameter is 75-250 micrometers is 60% or less of the whole and whose relative bulk density is 150-300 g/l. Relative bulk density specifies quantity of particles out of a range whose particle diameter is 75-250 micrometers to some extent. relative bulk density shall be not less than 150 g/l -- particle diameter -- small -- content of **** particles is stopped and it is easier to demonstrate an effect of having enlarged particle diameter. Since content of particles over 250 micrometers increases too much and it becomes severe with ZARA, precipitate silicic acid in which relative bulk density exceeds 300 g/l has the tendency to stop being suitable in use for the above-mentioned use.

[0012]Precipitate silicic acid of this invention is adding sodium hydroxide or a sodium silicate, and raises intensity of particles. Therefore, sodium hydroxide or a sodium silicate more than a constant rate exists in precipitate silicic acid. As that rule of thumb, pH when it is considered as suspension 4% can be used, and if this pH is 8.5 or more things, particle strength of a mentioned range can be obtained. If an addition of sodium hydroxide or a sodium silicate

increases too much, the dissolution of precipitate silicic acid will take place and it will also become the cause of changing the physical properties of precipitate silicic acid remarkably. Then, as for pH, when it is considered as suspension 4%, it is preferred that it is 11.5 or less. [0013] Hereafter, a manufacturing method of granular precipitate silicic acid of this invention is explained. Granular precipitate silicic acid of this invention can be manufactured by carrying out spray drying of the suspension obtained by adding sodium hydroxide or a sodium silicate to suspension of precipitate silicic acid, and adjusting the pH of said suspension to the range of 8.5-11.5. There is no restriction in particular in precipitate silicic acid used as a raw material. A manufacturing method of common precipitate silicic acid to below is explained. As an alkaline silicate which is reaction raw materials, generally a sodium silicate is used and it is preferred for this sodium silicate that a mole ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ uses 2.0-4.0. It is preferred to use sulfuric acid or chloride as mineral acid. A hydration precipitate silicic acid slurry is obtained by a method of adding sulfuric acid and a sodium silicate solution by predetermined time, controlling so that temperature and pH in this reaction vessel put in warm water and a sodium silicate solution and become a reaction vessel continuously fixed. Filtration and rinsing are performed and let this hydration precipitate silicic acid slurry be a humid cake. [0014] Suspension of precipitate silicic acid can be obtained by distributing water and slurring a humid cake obtained above. In this invention, a sodium silicate or sodium hydroxide is added to this suspension, and the pH of suspension is adjusted to the range of 8.5-11.5. The pH of suspension before pH adjustment is changing with amount of mineral acid used of reaction time of the aforementioned hydration precipitate silicic acid, etc., therefore adding a constant rate of sodium silicates or sodium hydroxide generally, and adjusting to desired pH is difficult for it. Therefore, monitoring the pH of suspension fully stirring suspension of precipitate silicic acid, a sodium silicate or sodium hydroxide is added and suspension of desired pH is obtained. Using sodium carbonate and sodium acetate can also adjust the pH of suspension to the above-mentioned range instead of a sodium silicate or sodium hydroxide. However, if suspension set as a predetermined range was used using sodium carbonate and sodium acetate, granular precipitate silicic acid of this invention cannot be obtained. [0015] When the pH of suspension by addition of sodium hydroxide or a sodium silicate is less than 8.5, granular precipitate silicic acid which has desired particle strength cannot be obtained. When an addition increases too much and pH exceeds 11.5, the dissolution of precipitate silicic acid starts and granular precipitate silicic acid of this invention cannot be obtained. When obtaining a hydration precipitate silicic acid slurry, straw matting which makes the pH of suspension of precipitate silicic acid 8.5 or more by lessening quantity of mineral acid for a reaction and maintaining the pH of slurry liquid highly at the time of ending reaction is possible. However, even if it dries precipitate silicic acid suspension in which pH of a prescribed range produced by doing in this way is shown like this invention, what has the same

particle strength as granular precipitate silicic acid of this invention is not obtained.

[0016]As for precipitate silicic acid to be used, in a manufacturing method of this invention, it is preferred to adjust a BET specific surface area in a reaction stage so that it may become the range of 150-400 m²/g. By making a BET specific surface area more than 150 m²/g, granular precipitate silicic acid which has desired particle strength can be obtained with an addition of comparatively few sodium hydroxide or sodium silicates. On the other hand, when a BET specific surface area becomes large, there is a tendency it to become difficult to obtain high-concentration precipitate silicic acid suspension. Then, as for a BET specific surface area, it is preferred that below 400 m²/g carries out.

[0017]Granular precipitate silicic acid is obtained by carrying out spray drying of the precipitate silicic acid suspension adjusted to the above-mentioned pH. In order to obtain granular precipitate silicic acid, a method of carrying out spray drying rather than a method of drying slowly like settlement desiccation is suitable. It is preferred to be able to use a publicly known spray dryer for spray drying, to be able to hold a nozzle type, a disk ceremony, etc. as spraying, and to use a nozzle-type spray dryer especially. In the case of a nozzle-type spray dryer, particle diameter is controllable by controlling a diameter of a spraying nozzle. Therefore, it is desirable to use a comparatively big thing of a nozzle diameter for obtaining granular precipitate silicic acid of this invention. Granular precipitate silicic acid can also change particle diameter by slurry concentration of suspension which carries out spray drying. In order to obtain granular precipitate silicic acid of desired particle diameter, it is appropriate to consider it, for example as 150-250 g/l of slurry concentration. Granular precipitate silicic acid which has desired particle diameter can be obtained by carrying out spray drying of the suspension in which a BET specific surface area adjusted slurry concentration to 150-250 g/l especially using suspension of precipitate silicic acid of 150-400 m²/g.

[0018]

[Example]Hereafter, an example and a comparative example are given and this invention is explained further. Measurement of the relative bulk density in an example and a comparative example, particle diameter, pH, and particle strength was performed by the following method.

[0019](I) It measured according to the umbrella examining method specified to 18 of measurement JISK5101 (the paints examining method) of relative bulk density.

(II) measuring the sample weight of each plus sieve, after setting the screen of 250, 200, 150, and 105 or 75-micrometer meshes of a net, putting in 50 g of samples using the measurement low tap type standard sieve shaker (made by Tsutsui Physicochemistry Apparatus company) of particle diameter and vibrating for 10 minutes -- the rate of the 75-250-micrometer range -- a table -- the bottom.

[0020](III) 100 ml of pH slurries of the measurement a slurry liquid of pH were taken to the

beaker, and it measured by the glass electrode pH meter by the concentration.

b) 2 g of samples were added to 50 ml of pondages of pHpH7 of a product, and it measured by the after-mixing glass electrode pH meter for 5 minutes.

(IV) Particle strength was measured using the measurement minute compression testing machine (the Shimadzu Corp. make / MCTM-2 type) of particle strength.

(V) The grade precipitate silicic acid sample of powdering was rubbed between the thumb and the index finger, and the grade of powdering was evaluated in accordance with the following standards.

O : it rolls, and a sex continues and is not powdered.

O : -- they are some particles -- although it breaks, it senses as granularity.

x: Particles are destroyed and particles are no longer accepted.

[0021]Adding and stirring 637 ml of the No. 3 sodium silicate solutions (Na_2O about 7%, SiO_2 about 22%) in 17,200 ml of warm water heated to Examples 1-3 and 190 ** of comparative examples. Subsequently, simultaneous pouring of 5,970 ml of the No. 3 sodium silicate solutions (it is the same as said concentration) and about 1,200 ml of the 48% sulfuric acid was carried out in 60 minutes so that the pH of reaction mixture might maintain 9-11. Sulfuric acid was poured 48 more% and reaction mixture was acidified. pH at the time of the end of acidification was set to about 3.0. The obtained sediment was filtered, warm water washed enough, and the humid cake was obtained. Water was made to distribute this humid cake, and slurry liquid was made so that slurry liquid concentration might be about 180 g/l. Next, the No. 3 sodium silicate solution (Na_2O about 4%, SiO_2 about 13%) was poured into this slurry liquid. After the amount of pouring poured 1.3%, 1.6%, and 1.9% respectively in the amount of Na_2O in a sodium silicate solution and measured the pH of the slurry liquid after 2-hour stirring to the solid content in slurry liquid, it dried using the nozzle type spray dryer, and obtained granular precipitate silicic acid. The comparative example 1 is sodium silicate an unadded thing. The measurement result of this product was shown in Table 1.

[0022]Adding and stirring 130 ml of the No. 3 sodium silicate solutions (Na_2O about 7%, SiO_2 about 22%) in 17,900 ml of warm water heated to Examples 4-6 and 260 ** of comparative examples. Subsequently, simultaneous pouring of 5,770 ml of the No. 3 sodium silicate solutions (it is the same as said concentration) and about 1,200 ml of the 48% sulfuric acid was carried out in 60 minutes so that the pH of reaction mixture might maintain 9-11. Sulfuric acid was poured 48 more% and reaction mixture was acidified. pH at the time of the end of acidification was set to about 3.0. The obtained sediment was filtered, warm water washed enough, and the humid cake was obtained. Water was made to distribute this humid cake, and slurry liquid was made so that slurry liquid concentration might be about 150 g/l. Next, sodium hydroxide solution was poured into this slurry liquid. After the amount of pouring poured 0.6%,

1.1%, and 1.6% respectively in the amount of Na_2O in a sodium hydroxide solution and measured the pH of the slurry liquid after 2-hour stirring to the solid content in slurry liquid, it dried using the nozzle type spray dryer, and obtained granular precipitate silicic acid. The comparative example 2 is sodium silicate an unadded thing. The measurement result of this product was shown in Table 1.

[0023] Water was made to distribute the humid cake obtained with the same reaction method as three to comparative example 4 Examples 1-3, and slurry liquid was made so that slurry liquid concentration might be about 180 g/l. Sodium carbonate solution was respectively poured 6% 2% in the amount of Na_2CO_3 to the solid content in slurry liquid 10% into this slurry liquid, slurry liquid pH after 2-hour stirring was measured, it dried using the nozzle type spray dryer, and granular precipitate silicic acid was obtained. The measurement result of this product was shown in Table 1.

[0024] Adding and stirring 355 ml of the No. 3 sodium silicate solutions (Na_2O about 7%, SiO_2 about 22%) in 16,000 ml of warm water heated to 590 °C of comparative examples. Subsequently, simultaneous pouring of 7,100 ml of the No. 3 sodium silicate solutions (it is the same as said concentration) and about 1,400 ml of the 48% sulfuric acid was carried out in 60 minutes so that the pH of reaction mixture might maintain 9-11. The sediment was filtered after the end of simultaneous pouring, without performing addition of sulfuric acid, warm water washed enough, and the humid cake was obtained. Water was made to distribute this humid cake, and slurry liquid was made so that slurry liquid concentration might be about 150 g/l. After measuring the pH of slurry liquid, it dried using the nozzle type spray dryer, and granular precipitate silicic acid was obtained. The measurement result of this product was shown in Table 1.

[0025] Add sulfuric acid to 19,600 ml of warm water heated to 660 °C of comparative examples 48%, and it is referred to as pH about 3.0. Subsequently, simultaneous pouring of 4,460 ml of the No. 3 sodium silicate solutions (Na_2O about 7%, SiO_2 about 22%) and about 940 ml of the 48% sulfuric acid was carried out in 60 minutes so that the pH of reaction mixture might maintain 2.5-3.5. Next, after carrying out temperature up to the degree of reaction liquid temperature of 90 °C and performing **** in addition for 4 hours until reaction mixture pH was set to about 9.0 in sodium hydroxide solution 23%, sulfuric acid was added 48% again and reaction mixture pH was set to about 3.0. The obtained sediment was filtered and rinsed and the humid cake was obtained. Slurry liquid was made so that water might be made to distribute this humid cake and slurry liquid concentration might be about 100 g/l, this slurry was dried using the nozzle type spray dryer, and granular precipitate silicic acid was obtained. The measurement result of this product was shown in Table 1.

[0026]

[Table 1]

	添 加 物	添 加 量 (%)	スラリー pH	製品 pH	粒子強度 (kgf/mm ²)	嵩 比 重 (g/l)	75~250 μ m 粒子 の占める割合 (%)	粉化の 程 度
比較例 1	—	—	5.50	6.30	0.03	230	78.6	×
実施例 1	ケイ酸ナトリウム	1.3	9.60	10.00	0.14	250	83.0	◎
" 2	"	1.6	10.00	10.30	0.17	250	82.7	◎
" 3	"	1.9	10.20	10.45	0.20	260	83.3	◎
比較例 2	—	—	5.80	6.70	0.08	240	70.5	○
実施例 4	水酸化ナトリウム	0.6	8.80	9.50	0.16	250	75.6	◎
" 5	"	1.1	9.50	9.95	0.20	250	76.2	◎
" 6	"	1.6	10.10	10.40	0.24	260	73.5	◎
比較例 3	炭酸ナトリウム	2.0	8.00	9.80	0.04	210	69.8	×
" 4	"	6.0	8.80	10.60	0.08	225	72.2	○
" 5	—	—	9.80	10.20	0.04	190	66.0	×
" 6	—	—	5.80	6.50	0.20	240	51.1	◎

[0027]

[Effect of the Invention] According to this invention, the granular precipitate silicic acid which has comparatively big particle diameter, does not powder during handling, and has the suitable touch and tactile feeling can be obtained. According to the manufacturing method of this invention, the particle strength of granular precipitate silicic acid can be controlled easily and freely, and the granular precipitate silicic acid which has desired particle strength can be obtained. Since granular precipitate silicic acid of this invention has good mobility and it is rare to powder during handling, it is effective in especially the industry dealt with in a large quantity. When using it as a bulking agent of rubber, it scours and the intrusion at the time of a lump demonstrates a good effect remarkable in shortening of working hours. Of course, it is effective also as bulking agents, such as a plastic and resin. Moderate viscosity can be maintained till use, without spoiling tactile feeling in inner mouth, without a granulation thing breaking during the time of toothbrushing manufacture, or preservation, when using it as a bulking agent of toothbrushing.

[Translation done.]